Part II – Quantum Mechanical Methods : Lecture 3

From Many-Body to Single-Particle: Quantum Modeling of Molecules

Jeffrey C. Grossman

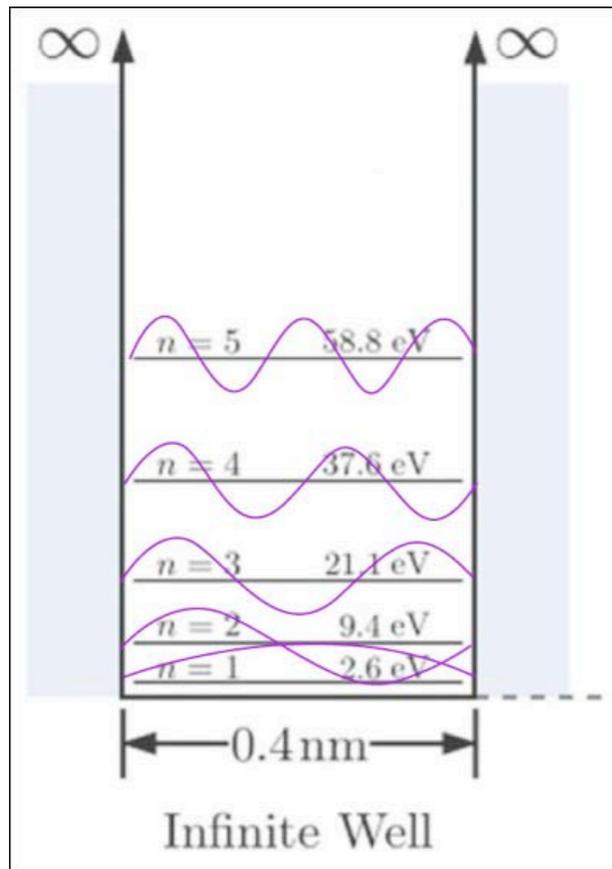Department of Materials Science and Engineering
Massachusetts Institute of Technology

Part II Topics

Motivation

∞   ∞

$n = 5$ 58.8 eV

$n = 4$ 37.6 eV

$n = 3$ 21.1 eV

$n = 2$ 9.4 eV

$n = 1$ 2.6 eV

—0.4 nm—

Infinite Well

Last time: 1-electron quantum mechanics to describe spectral lines

?
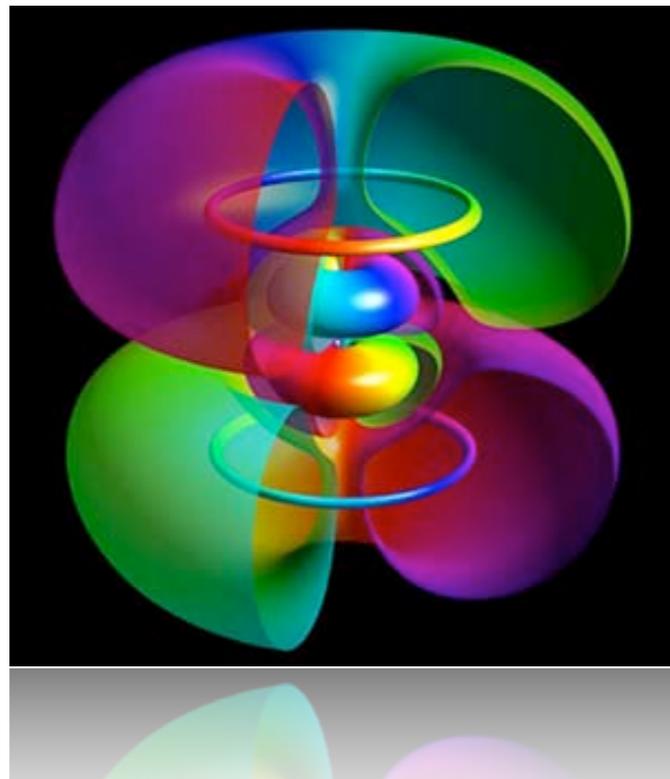
Today: many electrons to describe materials.

?

3

Lesson outline

- Review

- The Many-body Problem

- Hartree and Hartree-Fock

- Density Functional Theory

- Computational Approaches

- Modeling Software

- PWscf

Review: Schrödinger equation

H time independent: $\psi(\vec{r}, t) = \psi(\vec{r}) \cdot f(t)$

$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

$$\boxed{H\psi(\vec{r}) = E\psi(\vec{r})}$$

$$\psi(\vec{r}, t) = \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}Et}$$

time independent Schrödinger equation
stationary Schrödinger equation

Review: The hydrogen atom

stationary
Schrödinger equation

$$H\psi = E\psi$$

$$\left[\, T + V \,\right]\psi = E\psi$$

$$\left[\, -\frac{\hbar^2}{2m}\nabla^2 + V \right]\psi(\vec{r}) = E\psi(\vec{r})$$

just solve ☺

$$\left[\, -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right]\psi(\vec{r}) = E\psi(\vec{r})$$
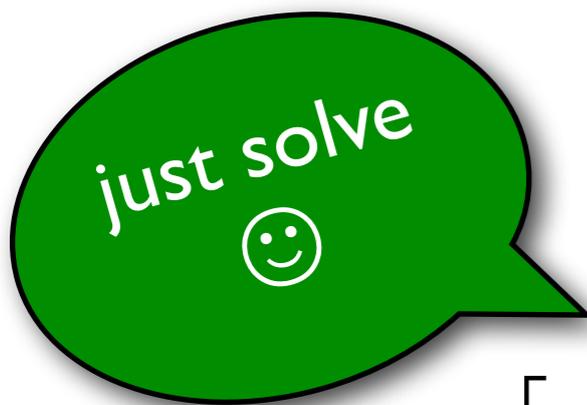
Radial Wavefunctions for a Coulomb V(r)

Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R^2_{nl}(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)\,a_0$, where a_0 is the first Bohr radius.

Images by MIT OpenCourseWare.

Angular Parts
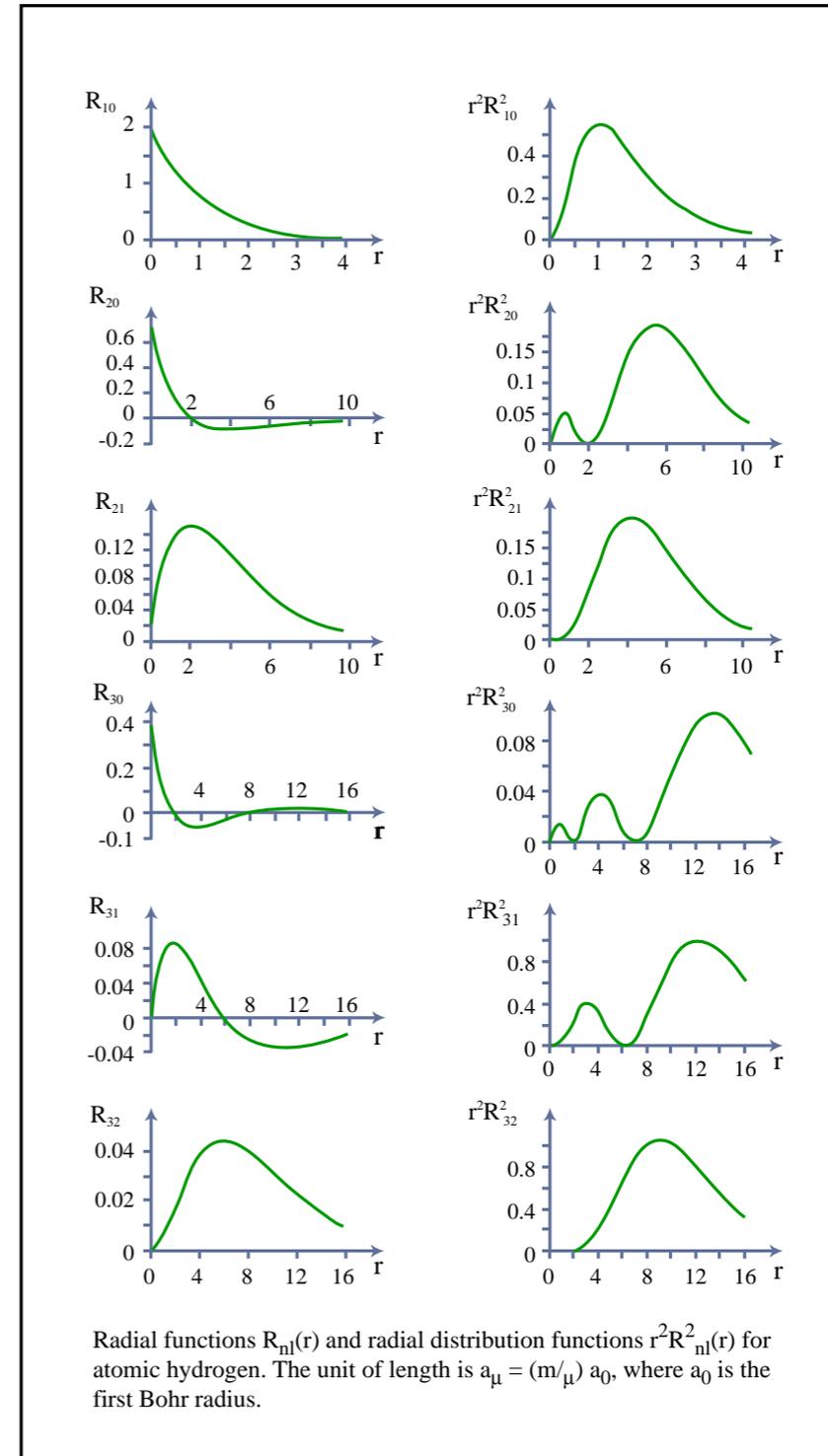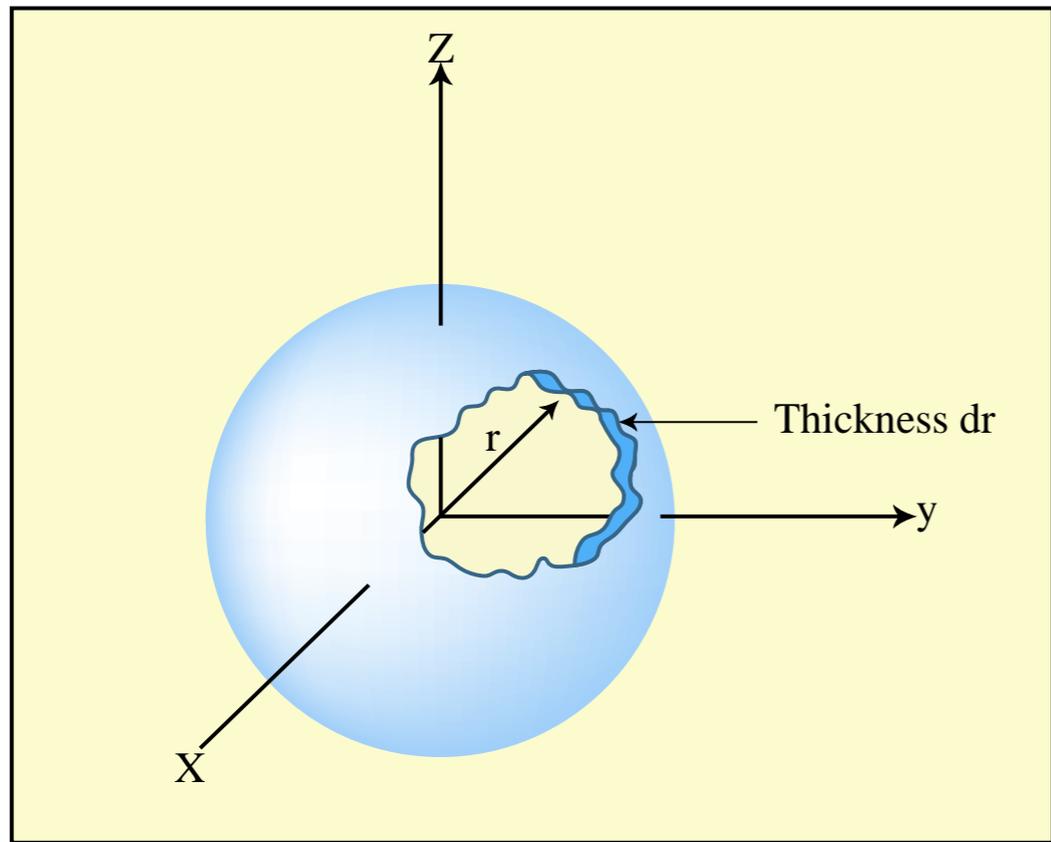
Image by MIT OpenCourseWare.
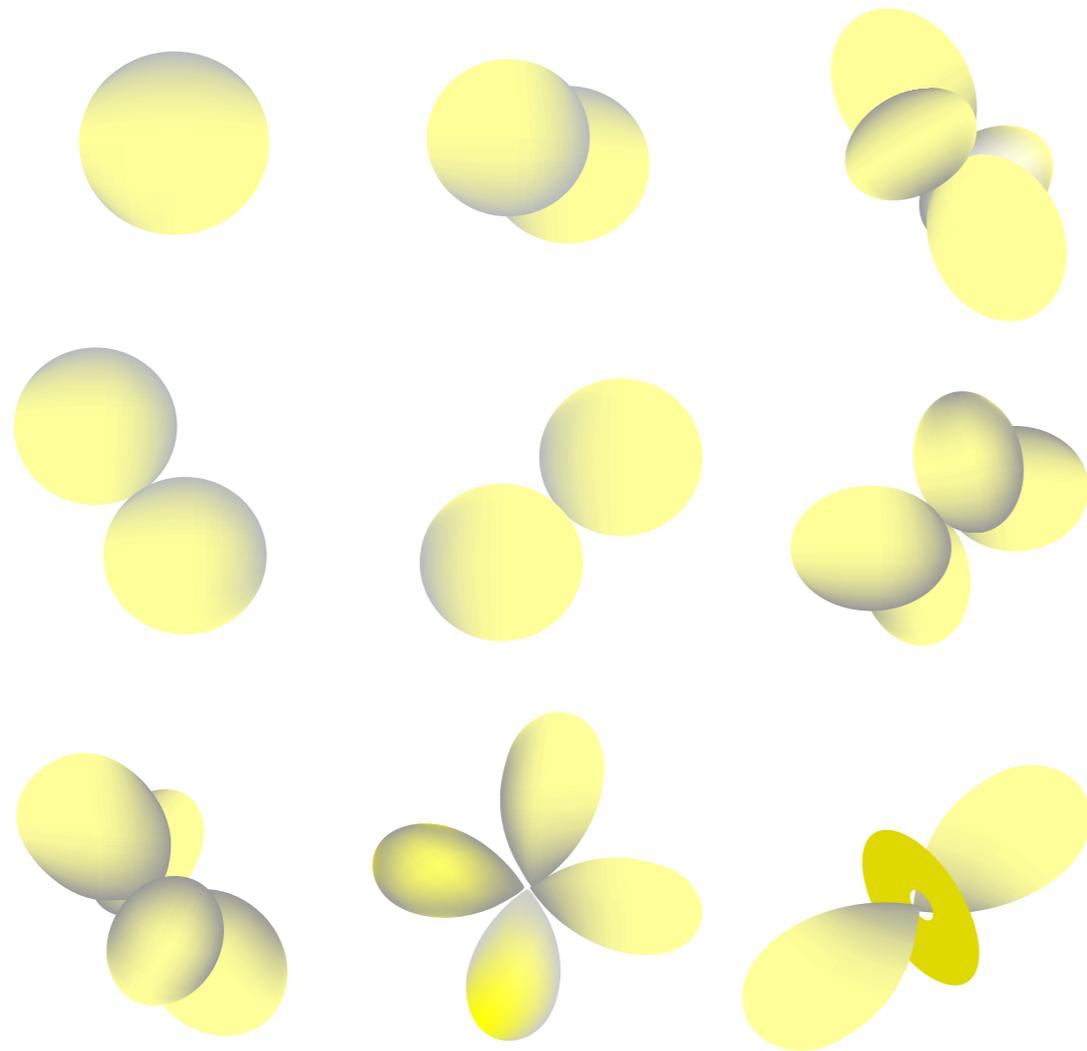
$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^{\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$$

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_2^{\pm 2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$$

$$Y_2^{\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$$

$$Y_2^0(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

Review: The hydrogen atom

quantum numbers

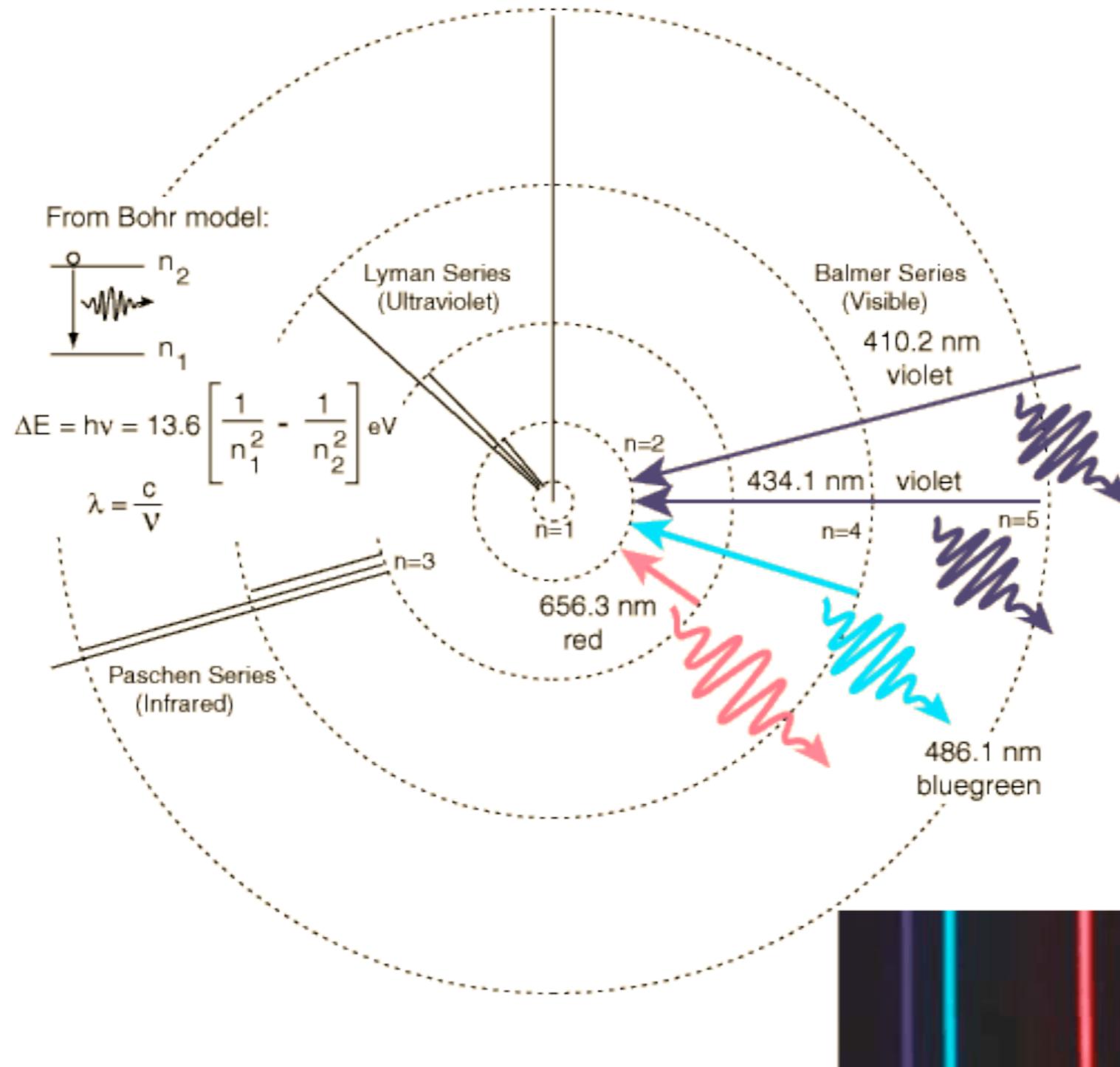| n	l	m_l	Atomic Orbital	$\psi_{n\,l\,m_l}(r, \theta, \phi)$
1	0	0	1s	$\dfrac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	2s	$\dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left[2 - \dfrac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	2p	$\dfrac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \dfrac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	± 1	2p	$\dfrac{1}{8\sqrt{\pi}\, a_0^{3/2}} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$

$$a_0 = \frac{\hbar^2}{me^2} = .0529 \text{ nm} = \text{first Bohr radius}$$

l and *m* versus *n*
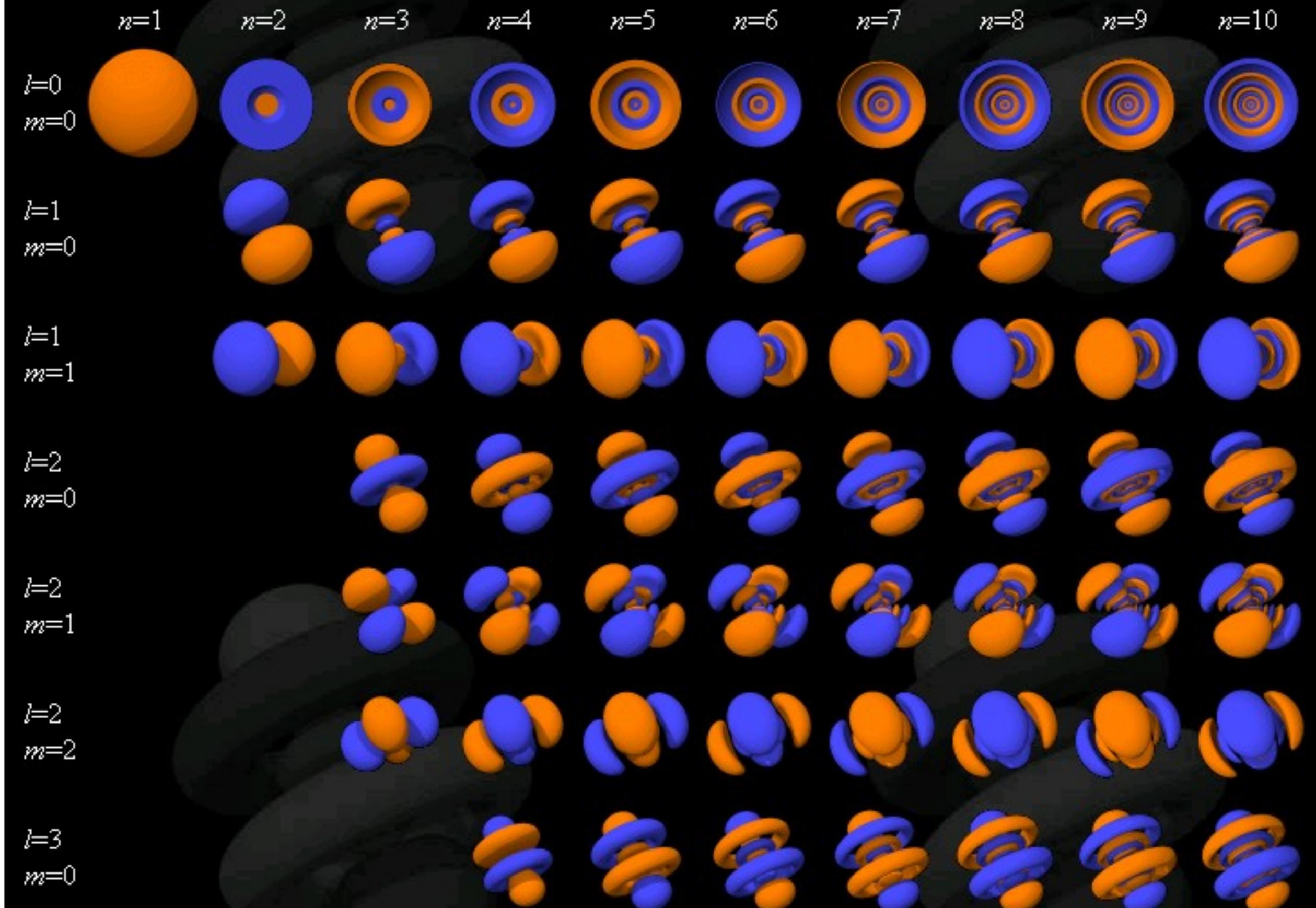
Courtesy of David Manthey. Used with permission. Source: http://www.orbitals.com/orb/orbtable.htm.

Review: The hydrogen atom

From Bohr model:

$$\Delta E = h\nu = 13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] eV$$

$$\lambda = \frac{c}{\nu}$$

Lyman Series
(Ultraviolet)

Balmer Series
(Visible)

410.2 nm
violet

434.1 nm   violet

n=2

n=1

n=4   n=5

n=3

656.3 nm
red

Paschen Series
(Infrared)

486.1 nm
bluegreen

Review: The hydrogen atom

Electron transitions for the Hydrogen atom

n=7
n=6
n=5
n=4
n=3
n=2
n=1

Brackett series
E(n) to E(n=4)

Paschen series
E(n) to E(n=3)

Balmer series
E(n) to E(n=2)

Lyman series
E(n) to E(n=1)
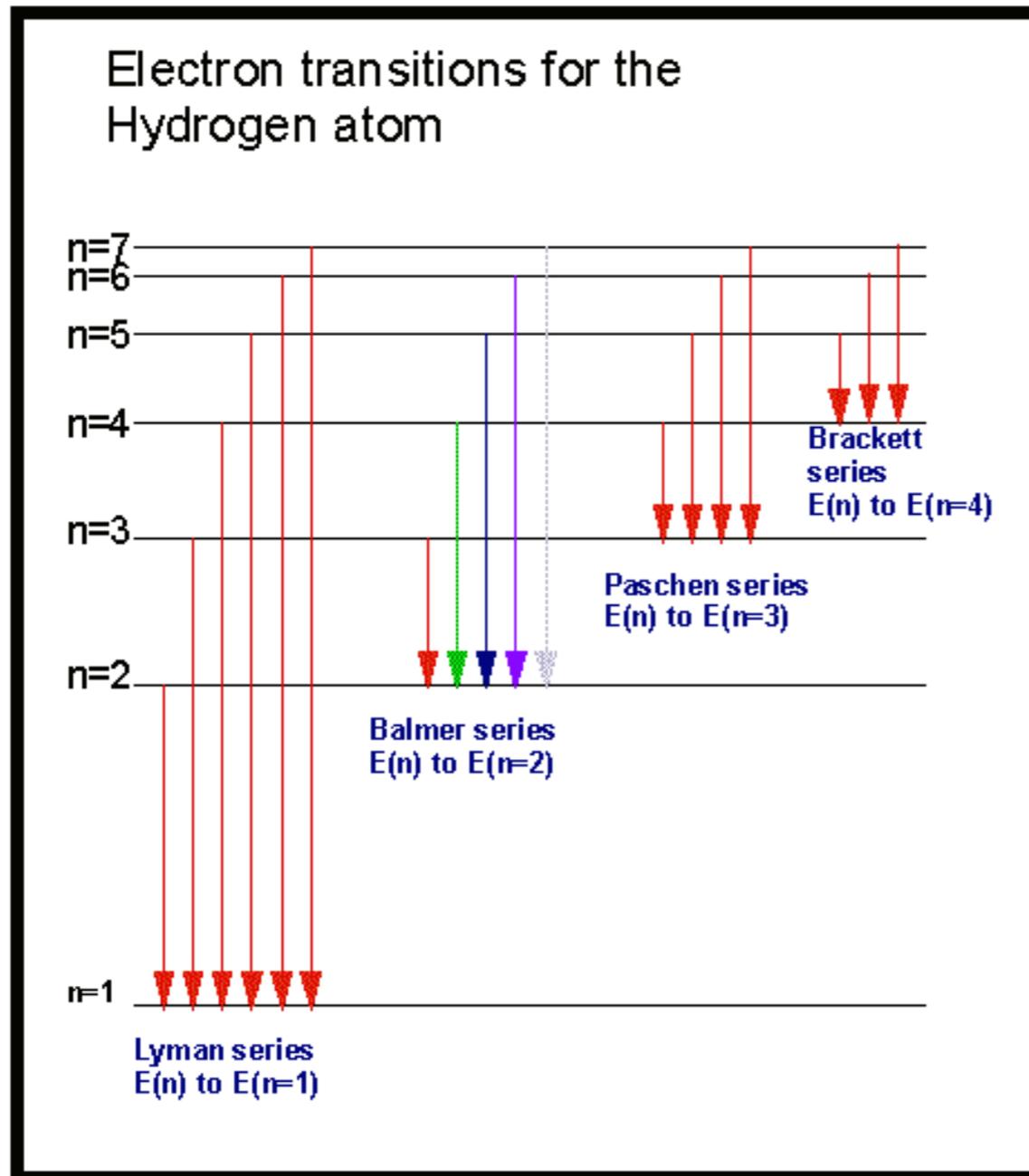
Continuum Spectrum

Emission Line Spectrum
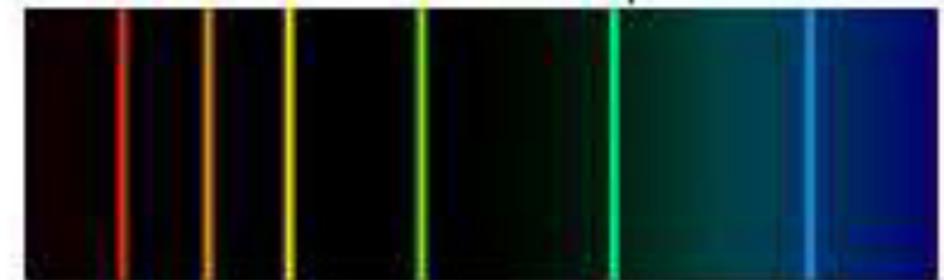
Absorption Line Spectrum
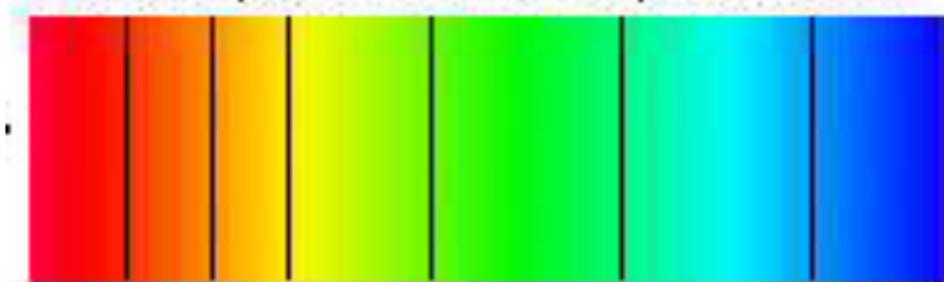
Review: Next? Helium

e⁻

r_1 r_{12}

+

r_2 e⁻
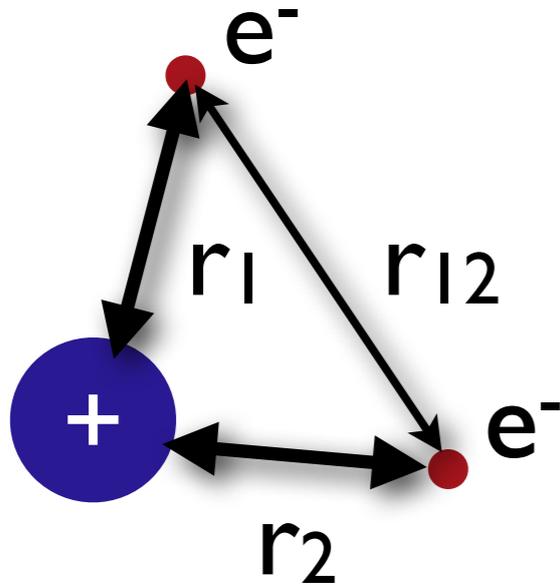
$$H\psi = E\psi$$

$$\left[H_1 + H_2 + W\right]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\left[T_1 + V_1 + T_2 + V_2 + W\right]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right]\psi(r_1, r_2) = E\psi(r_1, r_2)$$

cannot be solved analytically   problem!

Review: Spin

new quantum number: spin quantum number

for electrons: spin quantum number can ONLY be

up   down
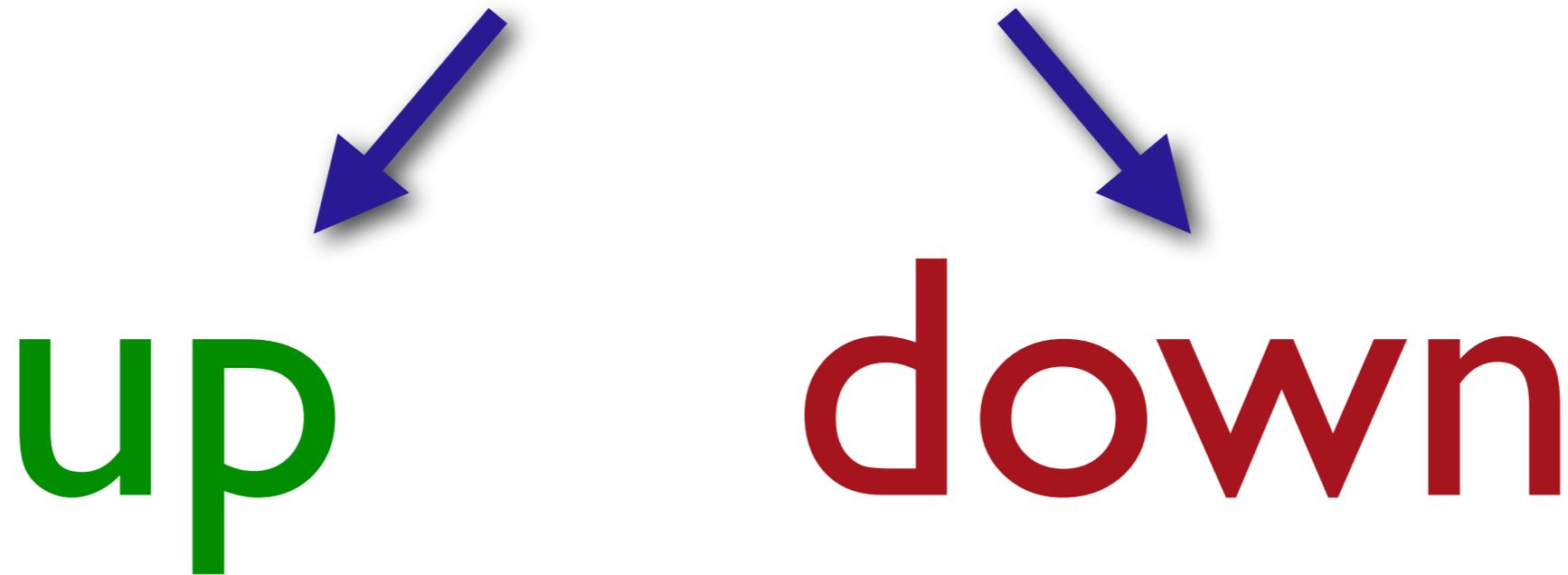
Everything is spinning ...

Stern–Gerlach experiment (1922)

$$\vec{F} = -\nabla E$$
$$= \nabla \, \vec{m} \cdot \vec{B}$$

Classical prediction

What was actually observed

Silver atoms

N

S

Inhomogeneous magnetic field

Furnace

Image courtesy of Teresa Knott.

Everything is spinning ...

In quantum mechanics particles can have
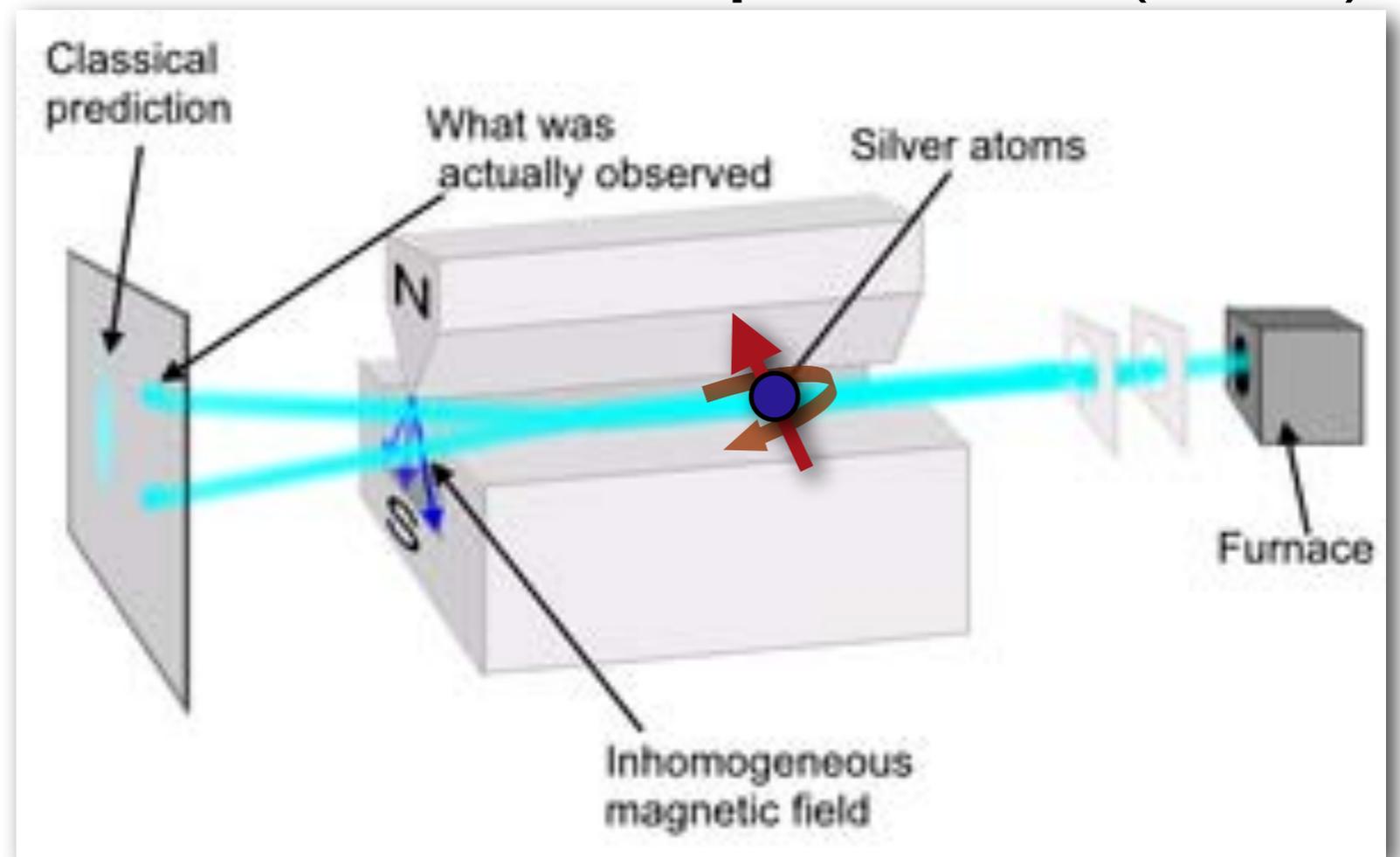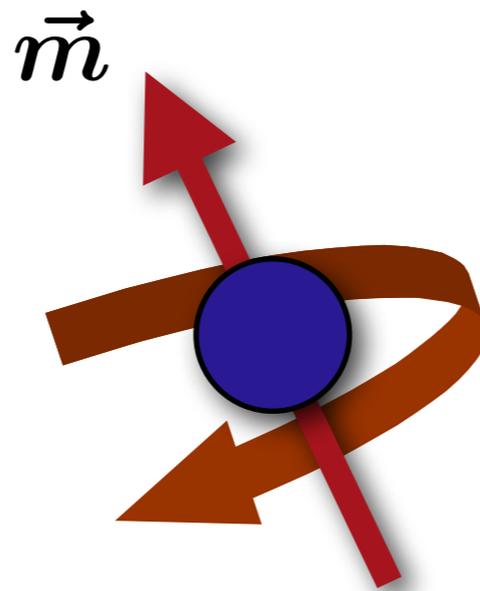a magnetic moment and a "spin"

magnetic
moment

$\vec{m}$

spinning
charge
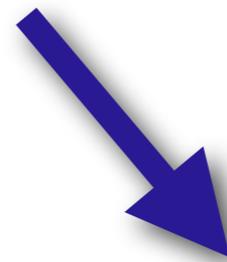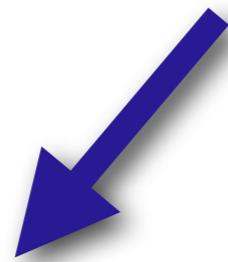
Everything is spinning ...

conclusion from the
Stern-Gerlach experiment

for electrons: spin can ONLY be

up   down

Spin History

Discovered in 1926 by Goudsmit and Uhlenbeck

I think you and Uhlenbeck have been very lucky to get your spinning electron published and talked about before Pauli heard of it. It appears that more than a year ago Kronig believed in the spinning electron and worked out something; the first person he showed it to was Pauli. Pauli ridiculed the whole thing so much that the first person became also the last and no one else heard anything of it. Which all goes to show that the infallibility of the Deity does not extend to his self-styled vicar on earth.

Part of a letter by L.H. Thomas to Goudsmit on March 25 1926 (source: Wikipedia).

Pauli's exclusions principle

Two electrons in a system cannot have the same quantum numbers!

hydrogen

quantum numbers:
main n: 1,2,3 ...
orbital l: 0,1,...,n-1
magnetic m: -l,...,l
spin: up, down

... ...
3s 3p 3d

2s 2p

1s
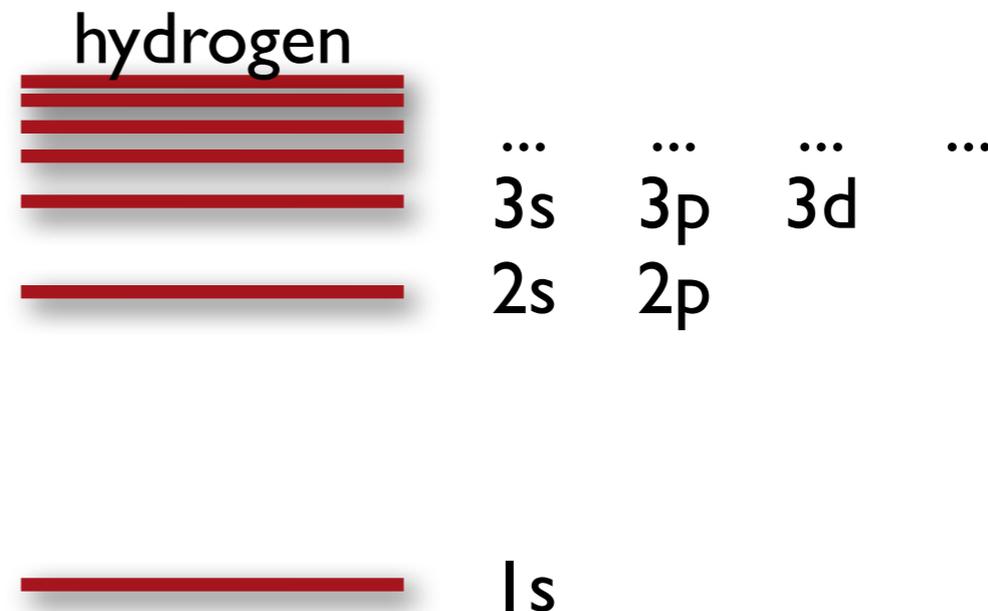
Pauli Exclusion Principle

"Already in my original paper I stressed the circumstance that I was unable to give a logical reason for the exclusion principle or to deduce it from more general assumptions. I had always the feeling, and I still have it today, that this is a deficiency."

W. Pauli, Exclusion Principle and Quantum Mechanics, Nobel prize acceptance lecture, Stockholm (1946).

Periodic table

This image is in the public domain. Source: Wikimedia Commons.

The many-body problem

helium: 2e⁻
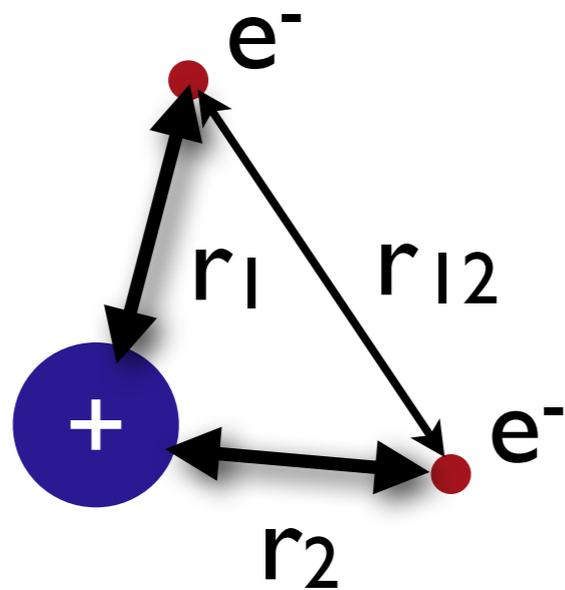
iron: 26e⁻
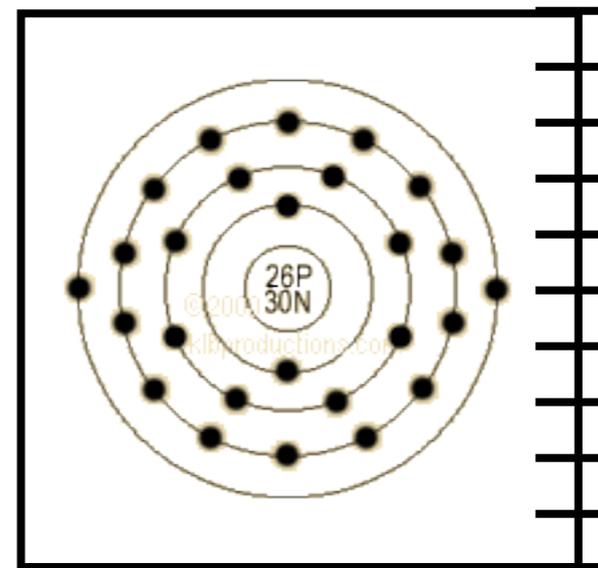
$$\psi = \psi(\vec{r}_1, \ldots, \vec{r}_n)$$

Dirac Quotes

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

P.A.M. Dirac, Proc. Roy. Soc. 123, 714 (1929)

...and in 1963

If there is no complete agreement […] between the results of one's work and the experiment, one should not allow oneself to be too discouraged […]

P.A.M. Dirac, Scientific American, May 1963

The Multi-Electron Hamiltonian

$$H\psi = E\psi$$

Remember the good old days of the 1-electron H-atom??

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r) = E\psi(r)$$

They're over!

$$H = -\sum_{\substack{i=1}}^{N}\frac{h^2}{2M_i}\nabla^2_{\mathbf{R}_i} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\i\neq j}}^{N}\frac{Z_iZ_je^2}{|\mathbf{R}_i-\mathbf{R}_j|} - \frac{h^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_ie^2}{|\mathbf{R}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\i\neq j}}^{n}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}$$

kinetic energy of ions

potential energy of ions

kinetic energy of electrons

electron-electron interaction

electron-ion interaction

Multi-Atom-Multi-Electron Schrödinger Equation

$$H(\mathbf{R}_1,...,\mathbf{R}_N;\mathbf{r}_1,...,\mathbf{r}_n)\,\Psi(\mathbf{R}_1,...,\mathbf{R}_N;\mathbf{r}_1,...,\mathbf{r}_n) = E\,\Psi(\mathbf{R}_1,...,\mathbf{R}_N;\mathbf{r}_1,...,\mathbf{r}_n)$$

Born-Oppenheimer Approximation

Source: Discover Magazine Online
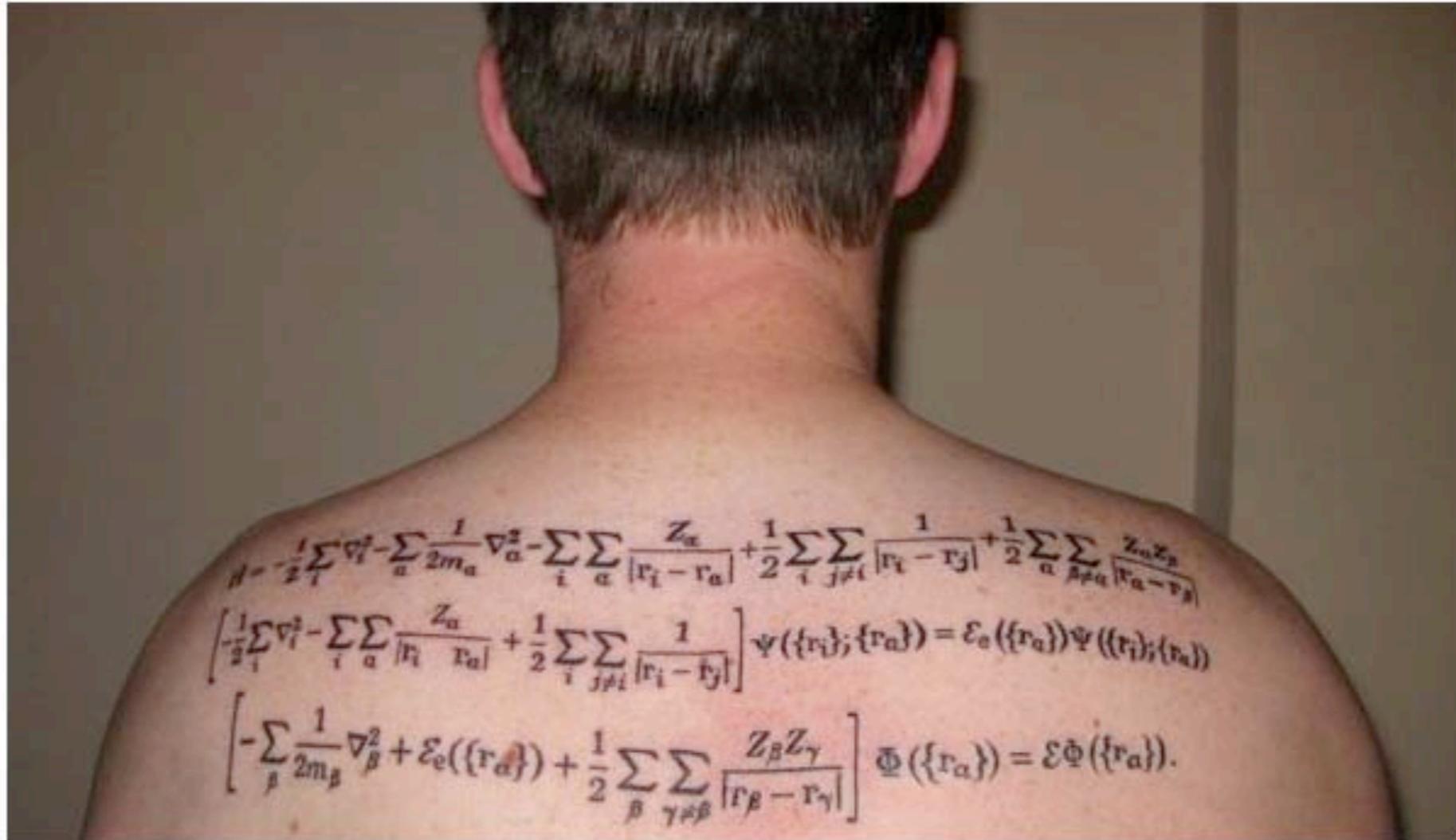
Joe writes, "My tattoo is 3 lines of equations, the top is the Born Oppenheimer Approximation, the second line is the equation in the form of a 3-Dimensional Schroedinger Equation, and the solution in the form of a Schroedinger Equation. As a biochemist and molecular biophysicist I studied a lot of this stuff and I must say, Schroedinger was my favorite and well, I had to do it. The ink was done at Red Sky Studios in Tucson, AZ by artist Lisa."

Born-Oppenheimer Approximation (skinless version)

- mass of nuclei exceeds that of the electrons by a factor of 1000 or more
- we can neglect the kinetic energy of the nuclei
- treat the ion-ion interaction classically
- significantly simplifies the Hamiltonian for the electrons:

Born   Oppenheimer

This term is just an external potential $V(r_j)$

$$H = -\frac{h^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{\left|\mathbf{R}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i \neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

Solutions

quantum chemistry

density functional theory

Moller-Plesset perturbation theory MP2

coupled cluster theory CCSD(T)
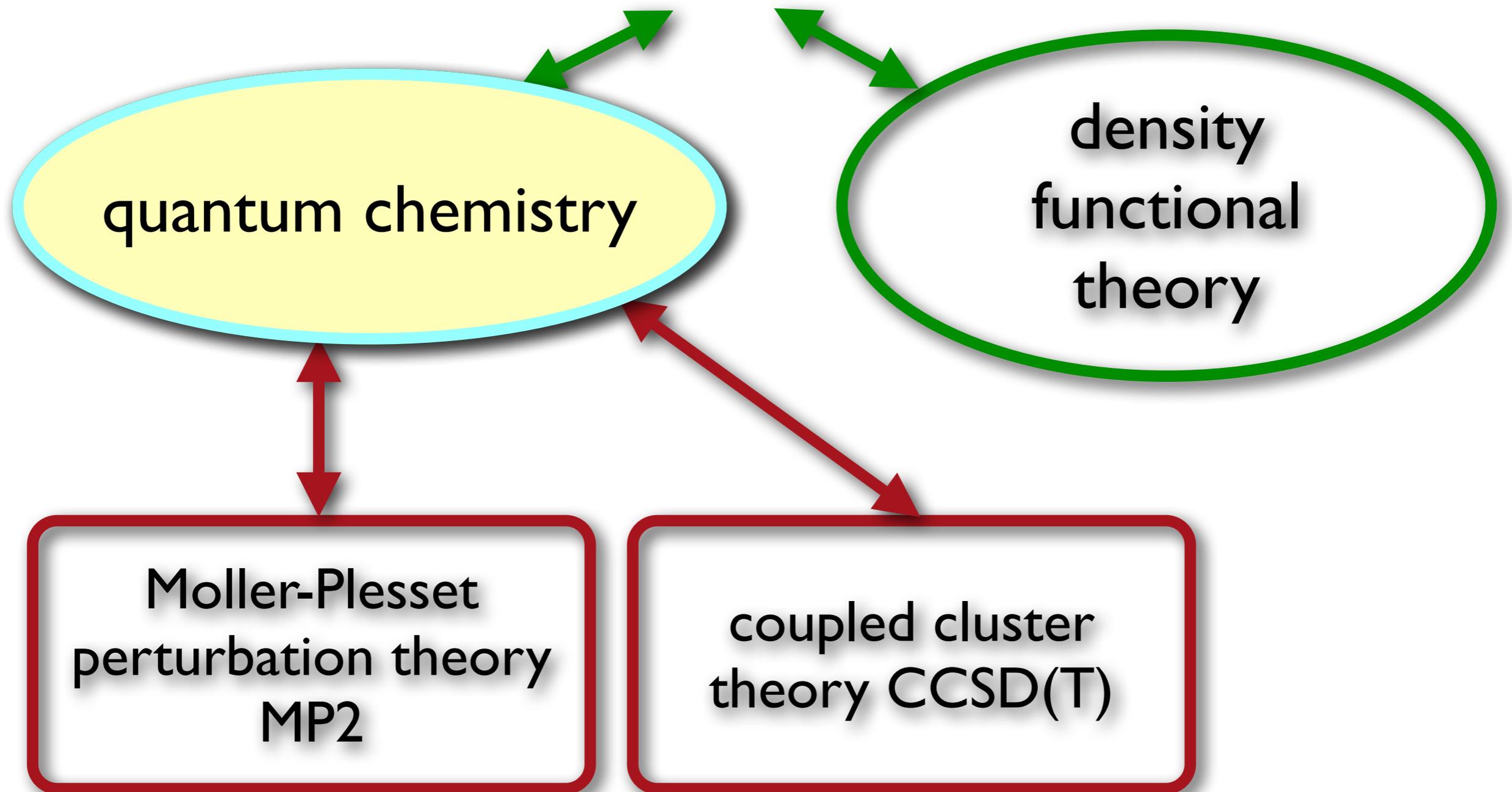
Hartree Approach

Write wavefunction as a simple product of single particle states:

$$\Psi\left(\mathbf{r}_1,...,\mathbf{r}_n\right) = \psi_1\left(\mathbf{r}_1\right)\psi_2\left(\mathbf{r}_2\right)...\psi_n\left(\mathbf{r}_n\right)$$

Hard Product of Easy

Leads to an equation we can solve on a computer!

$$\left\{-\frac{h^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{\substack{j=1\\j\neq i}}^{n}\int d\mathbf{r}\,\frac{e^2\left|\psi_j(\mathbf{r})\right|^2}{\left|\mathbf{r}_j - \mathbf{r}\right|}\right\}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

28

Hartree Approach

$$\left\{ -\frac{h^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{n} \int d\mathbf{r}\, \frac{e^2 \left|\psi_j(\mathbf{r})\right|^2}{\left|\mathbf{r}_j - \mathbf{r}\right|} \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

The solution for each state depends on all the other states (through the Coulomb term).

- we don't know these solutions a priori
- must be solved iteratively:
  - guess form for { $\Psi_i^{\text{in}}(\mathbf{r})$ }
  - compute single particle Hamiltonians
  - generate { $\Psi_i^{\text{out}}(\mathbf{r})$ }
  - compare with old
    - if different set { $\Psi_i^{\text{in}}(\mathbf{r})$ } = { $\Psi_i^{\text{out}}(\mathbf{r})$ } and repeat
    - if same, you are done
- obtain the self-consistent solution

Simple Picture...But...

Interacting

Non-Interacting
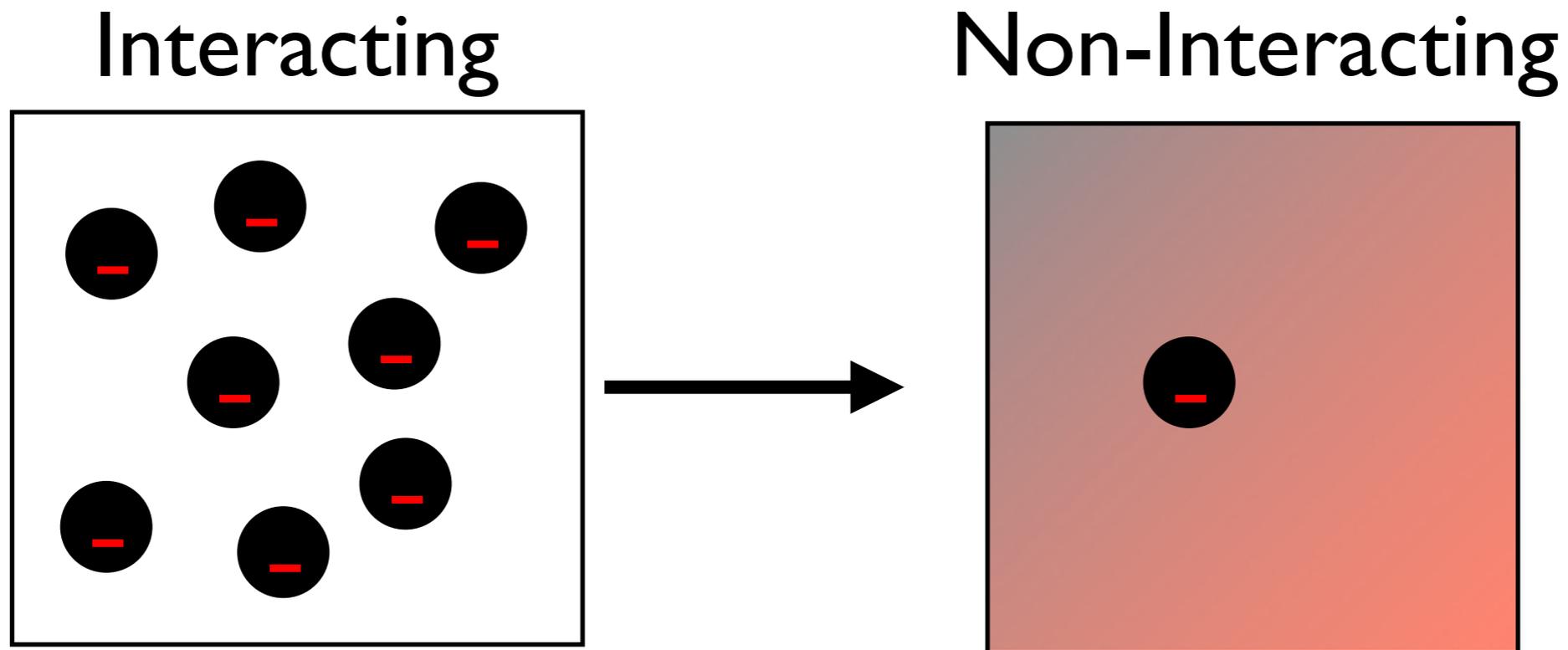
After all this work, there is still one major problem:
the solution is fundamentally wrong

The fix brings us back to spin!

Symmetry Holds the Key

Speculation: everything we know with scientific certainty is somehow dictated by symmetry.

The relationship between symmetry and quantum mechanics is particularly striking.

Exchange Symmetry

- all electrons are *indistinguishable*
  - electrons that made da Vinci, Newton, and Einstein who they were, are *identical* to those within our molecules
    a bit humbling...

- so if
  - I show you a system containing electrons
  - you look away
  - I exchange two electrons in the system
  - you resume looking at system
  - there is no experiment that you can conduct that will indicate that I have switched the two electrons

Mathematically

- define the exchange operator:
$$\chi_{12}\,\psi_1(r_1)\,\psi_2(r_2) = \psi_1(r_2)\,\psi_2(r_1)$$

- exchange operator eigenvalues are ±1:

$$\text{suppose } \hat{\chi}_{12}\,\phi = \chi\phi$$

$$\hat{\chi}_{12}\,\hat{\chi}_{12}\,\phi = \chi^2\phi = \phi$$

$$\chi^2 = 1, \text{ or } \chi = \pm 1.$$

Empirically

- all quantum mechanical states are also eigenfunctions of exchange operators
    - those with eigenvalue 1 (symmetric) are known as Bosons
    - those with eigenvalue -1 (antisymmetric) are known as Fermions
- profound implications for materials properties
    - wavefunctions for our many electron problem must be anti-symmetric under exchange
    - implies Pauli exclusion principle

Hartree-Fock

- Employing Hartree's approach, but
    - enforcing the anti-symmetry condition
    - accounting for spin
- Leads to a remarkable result:

$$\left\{-\frac{\mathrm{h}^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + \sum_{\substack{j=1 \\ j\neq i}}^{n}\int d\mathbf{r}\,\frac{e^2\left|\psi_j(\mathbf{r})\right|^2}{\left|\mathbf{r}_j - \mathbf{r}\right|}\right\}\psi_i(\mathbf{r}) - \sum_{\substack{j=1 \\ j\neq i}}^{n}\delta_{s_i,s_j}\int d\mathbf{r}'\,\frac{e^2}{\left|\mathbf{r}'-\mathbf{r}\right|}\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- Hartree-Fock theory is the foundation of molecular orbital theory.
- It is based upon a choice of wavefunction that guarantees antisymmetry between electrons.

it's an emotional moment....

But...Hartree-Fock

- neglects important contribution to electron energy (called "correlation" energy)

- difficult to deal with: integral operator makes solution complicated

- superceded by another approach: density functional theory

Solutions

quantum chemistry

density functional theory

Moller-Plesset perturbation theory MP2

coupled cluster theory CCSD(T)
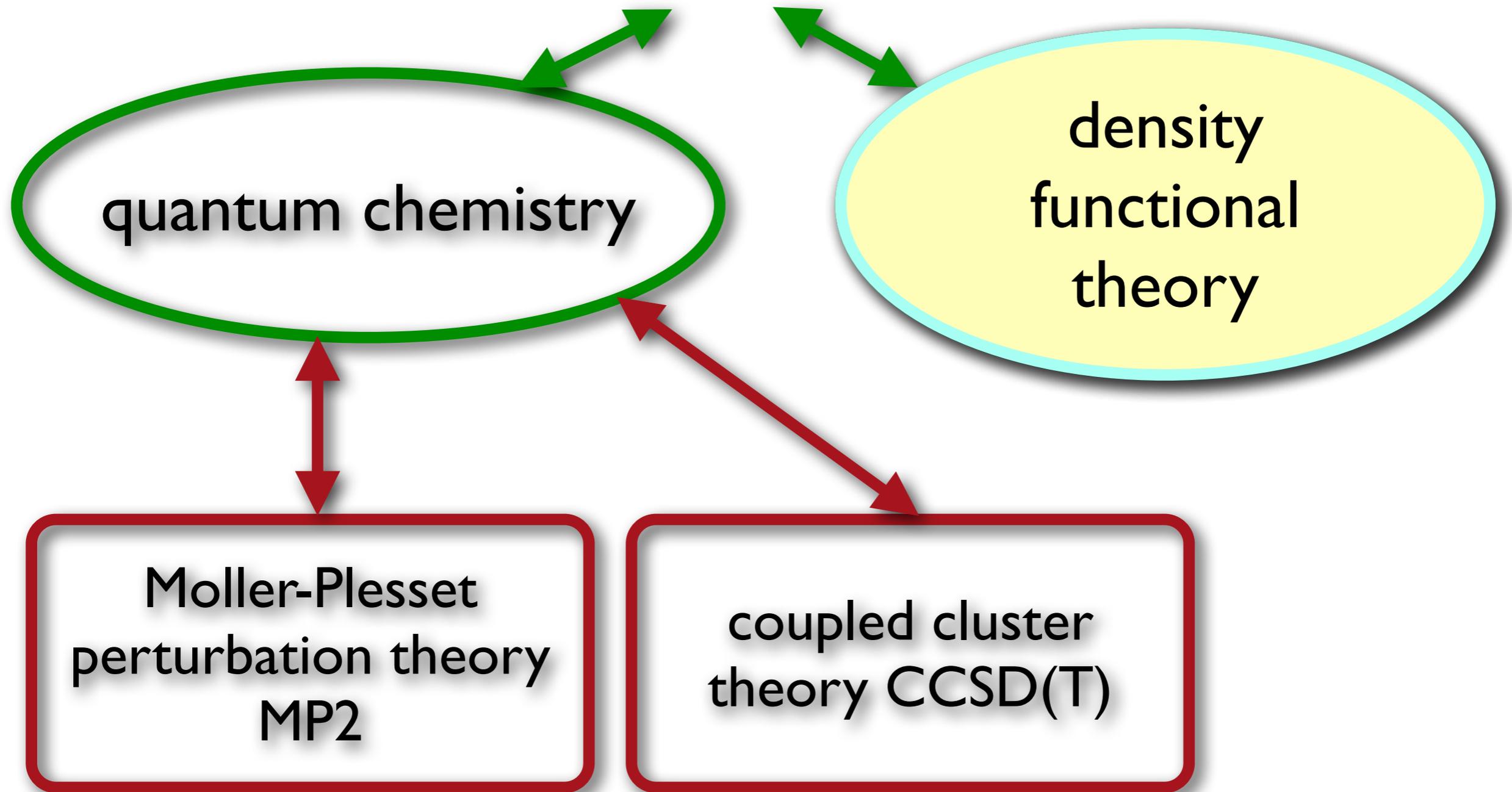
Solving the Schrodinger Equation
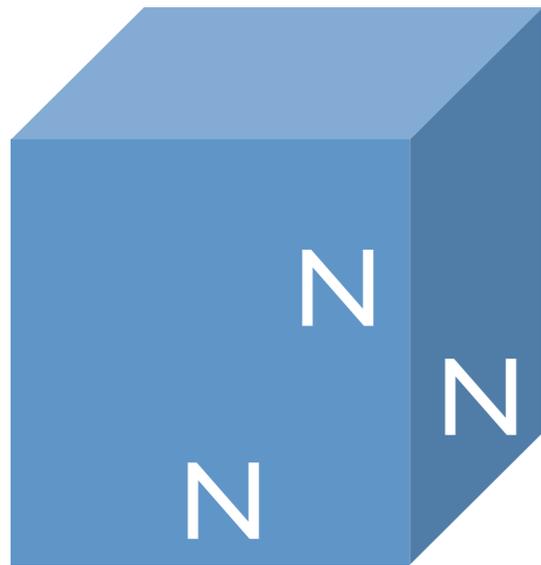
No matter how you slice it, the wavefunction is a beast of an entity to have to deal with.

For example: consider that we have n electrons populating a 3D space.

Let's divide 3D space into NxNxN=2x2x2 grid points.

To reconstruct $\Psi(r)$, how many points must we keep track of?

Solving the Schrodinger Eq.

divide 3D space into NxNxN=2x2x2 grid points
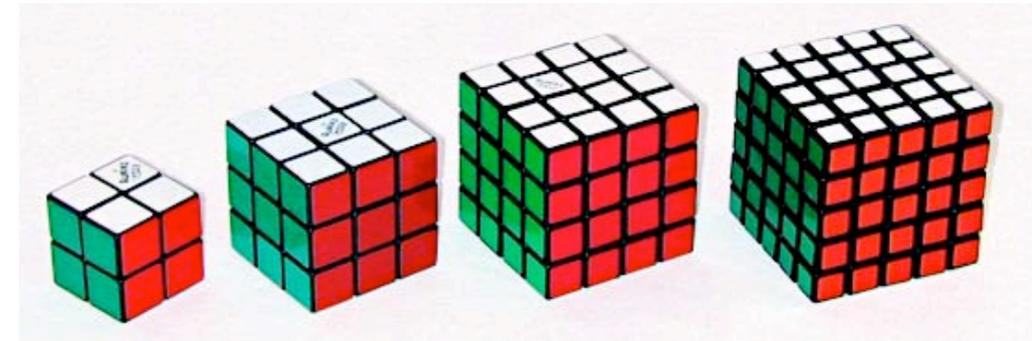
$$\Psi = \Psi(r_1, \ldots, r_n) \qquad \text{\# points} = N^{3n}$$

n=# electrons	$\Psi(N^{3n})$
1	8
10	10^9
100	10^{90}
1,000	10^{900}

Working with the Density

The electron density seems to be a more manageable quantity.

Wouldn't it be nice if we could reformulate our problem in terms of the density, rather than the wavefunction?

Energy $\longleftrightarrow$ Electron Density

$$E_0 = E[n_0]$$

Walter Kohn (left), receiving the Nobel prize in chemistry in 1998.

Why DFT?

computational expense for system size N:

Quantum Chemistry methods; MP2, CCSD(T) $\longrightarrow$ $O(N^5\text{-}N^7)$

Density Functional Theory $\longrightarrow$ $O(N^3); O(N)$

Example

silicon
2 atoms/unit cell

DFT: 0.1 sec   CCSD(T): 0.1 sec

MP2: 0.1 sec

silicon
100 atoms/unit cell

DFT: 5 hours   CCSD(T): 2000 years!!!

MP2: 1 year
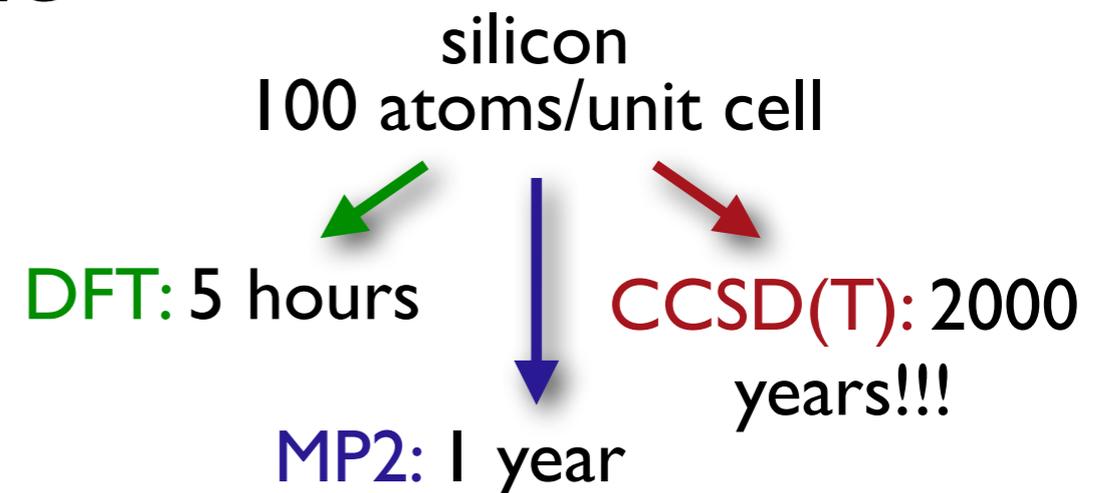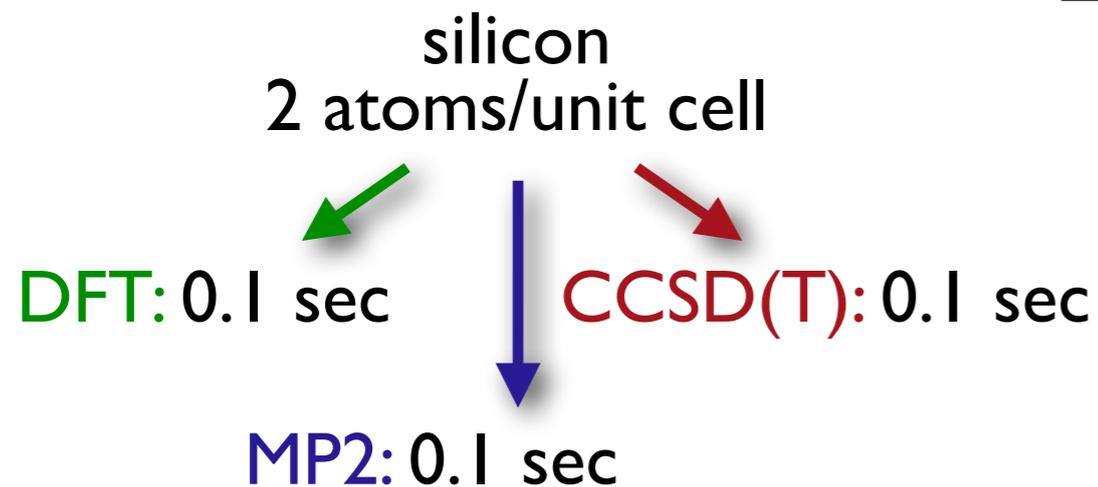
Why DFT?

Image by MIT OpenCourseWare.

Density functional theory

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

wave function: complicated!

$$n = n(\vec{r})$$

electron density: easy!

Walter Kohn

DFT 1964

Density functional theory

electron density n

ion
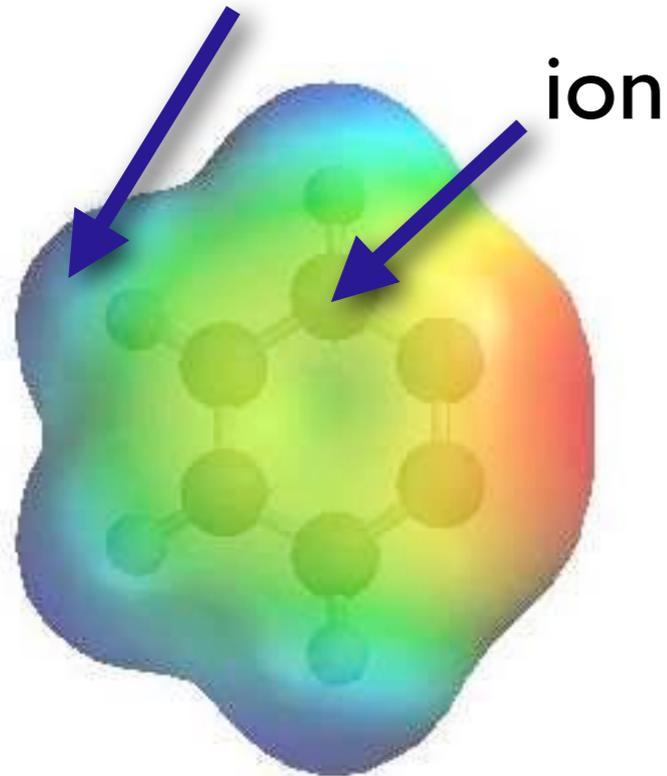
Total energy is a functional of the electron density.

$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic

ion-electron

ion-ion

electron-electron

Density functional theory

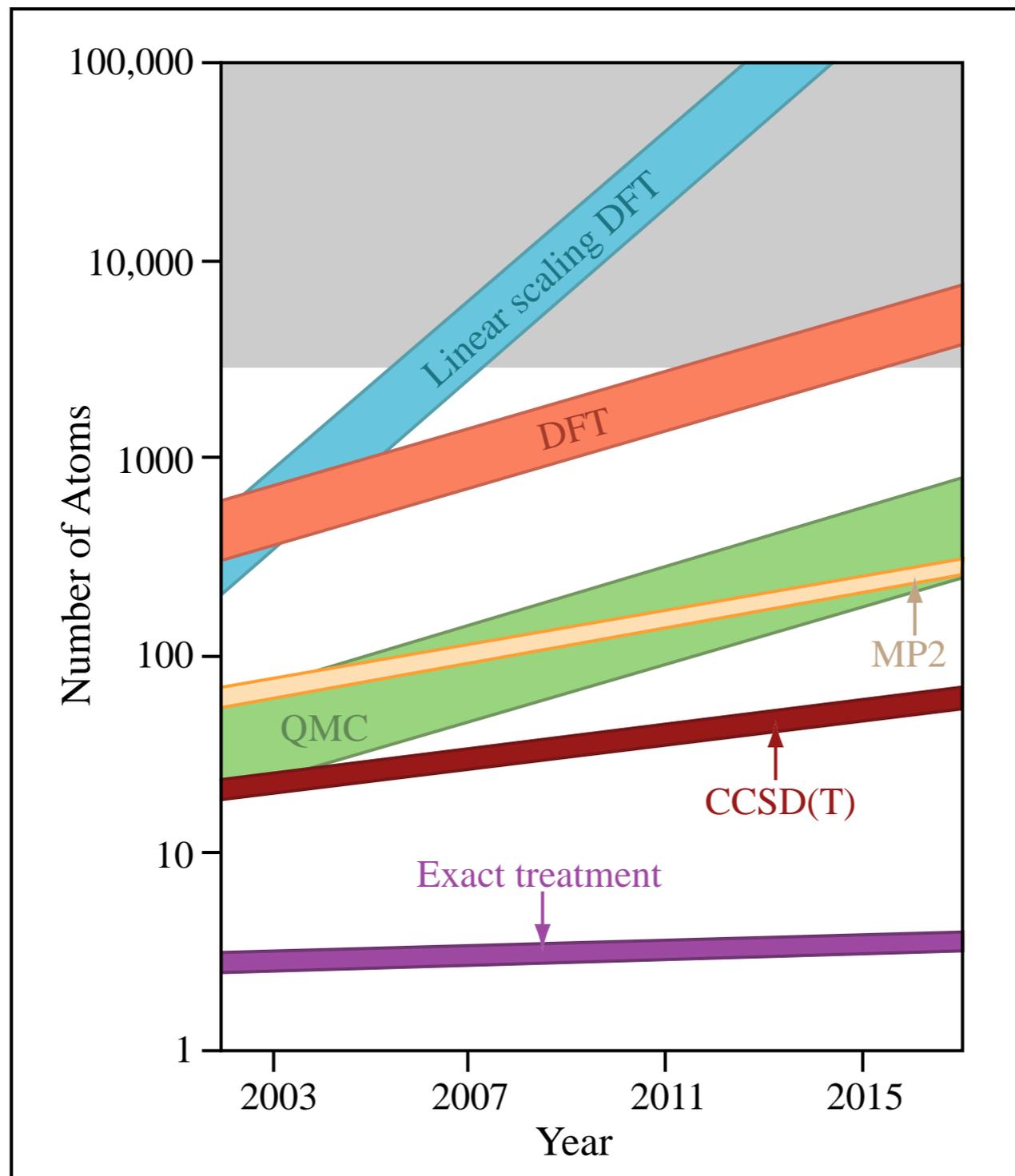$$E[n] = T[n] + V_{ii} + V_{ie}[n] + V_{ee}[n]$$

kinetic   ion-ion   ion-electron   electron-electron

electron density $\quad n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$

$$E_{\text{ground state}} = \min_\phi E[n]$$

Find the wave functions that minimize the energy using a functional derivative.

Density Functional Theory

Finding the minimum leads to
Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

ion potential   Hartree potential   exchange-correlation potential

equations for non-interacting electrons

Density functional theory

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

Only one problem: v_{xc} not known!

approximations necessary

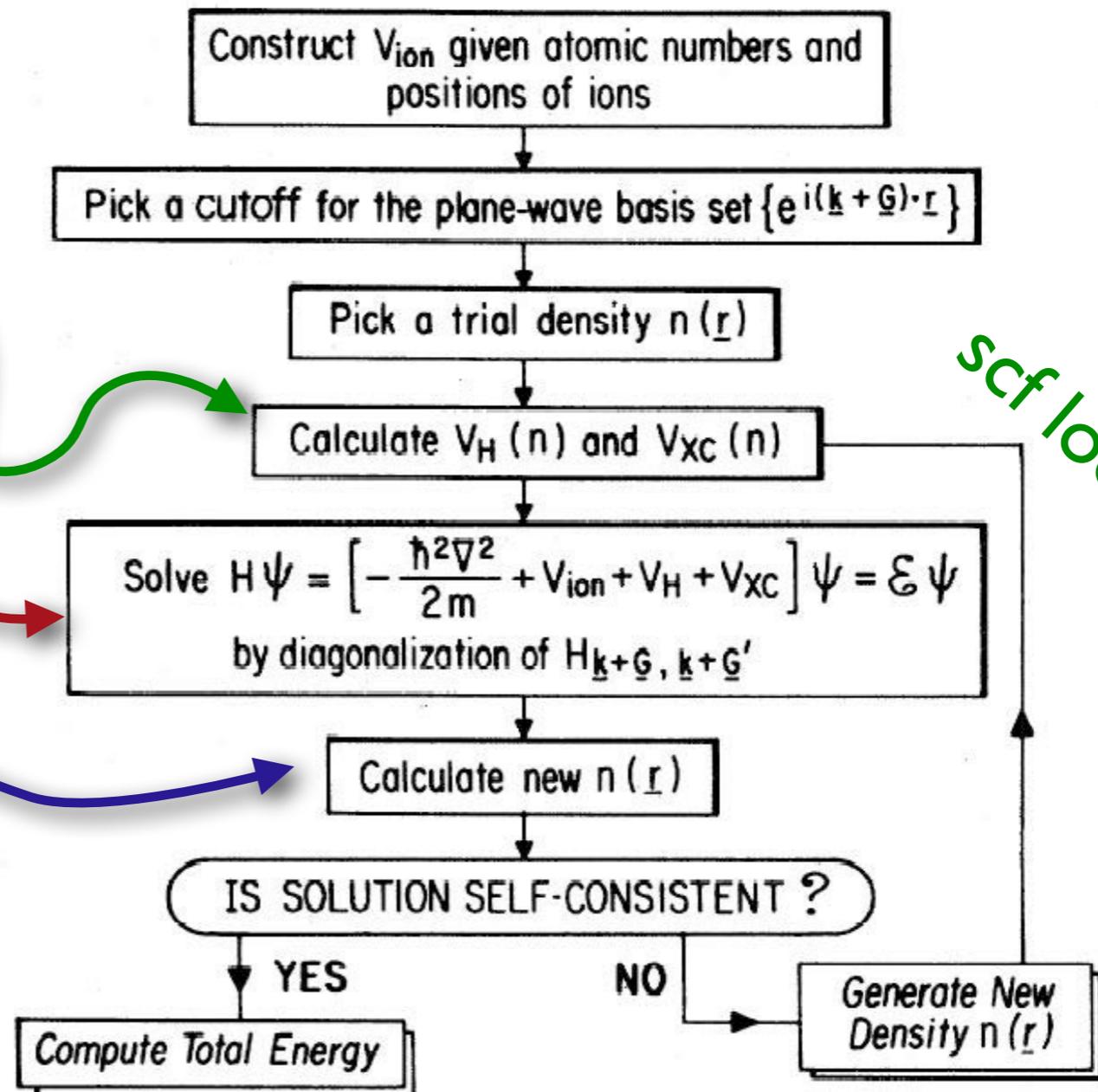local density
approximation
LDA

general gradient
approximation
GGA

Self-consistent cycle

Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}),$$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

Construct V_{ion} given atomic numbers and positions of ions

Pick a cutoff for the plane-wave basis set $\{e^{i(\underline{k}+\underline{G})\cdot\underline{r}}\}$

Pick a trial density $n(\underline{r})$

Calculate $V_H(n)$ and $V_{XC}(n)$

Solve $H\psi = \left[-\frac{\hbar^2\nabla^2}{2m} + V_{ion} + V_H + V_{XC} \right]\psi = \mathcal{E}\psi$ by diagonalization of $H_{\underline{k}+\underline{G},\,\underline{k}+\underline{G}'}$

scf loop

Calculate new $n(\underline{r})$

IS SOLUTION SELF-CONSISTENT ?

YES   NO

Compute Total Energy

Generate New Density $n(\underline{r})$

Modeling software

name	license	basis functions	pro/con
ABINIT	free	plane waves	very structured
ONETEP	pay	Wannier functions	linear scaling
Wien2k	pay	Y_{lm} + plane waves	very accurate
VASP	pay	plane waves	fast
PWscf	free	plane waves	fast

Basis functions

Matrix eigenvalue equation:

$$\psi = \sum_i c_i \phi_i$$

expansion in orthonormalized basis functions

$$H\psi = E\psi$$

$$H \sum_i c_i \phi_i = E \sum_i c_i \phi_i$$

$$\int d\vec{r}\, \phi_j^* H \sum_i c_i \phi_i = E \int d\vec{r}\, \phi_j^* \sum_i c_i \phi_i$$

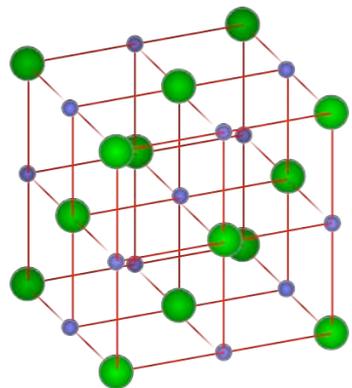$$\sum_i H_{ji} c_i = E c_j$$

$$\mathcal{H}\vec{c} = E\vec{c}$$

Plane waves as basis functions

plane wave expansion:

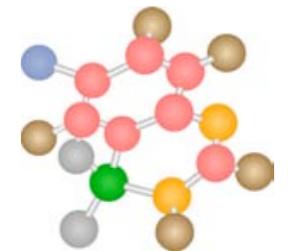$$\psi(\vec{r}) = \sum_j c_j \boxed{e^{i\vec{G}_j \cdot \vec{r}}}$$

plane wave

Cutoff for a maximum G is necessary and results in a finite basis set.

Plane waves are periodic,
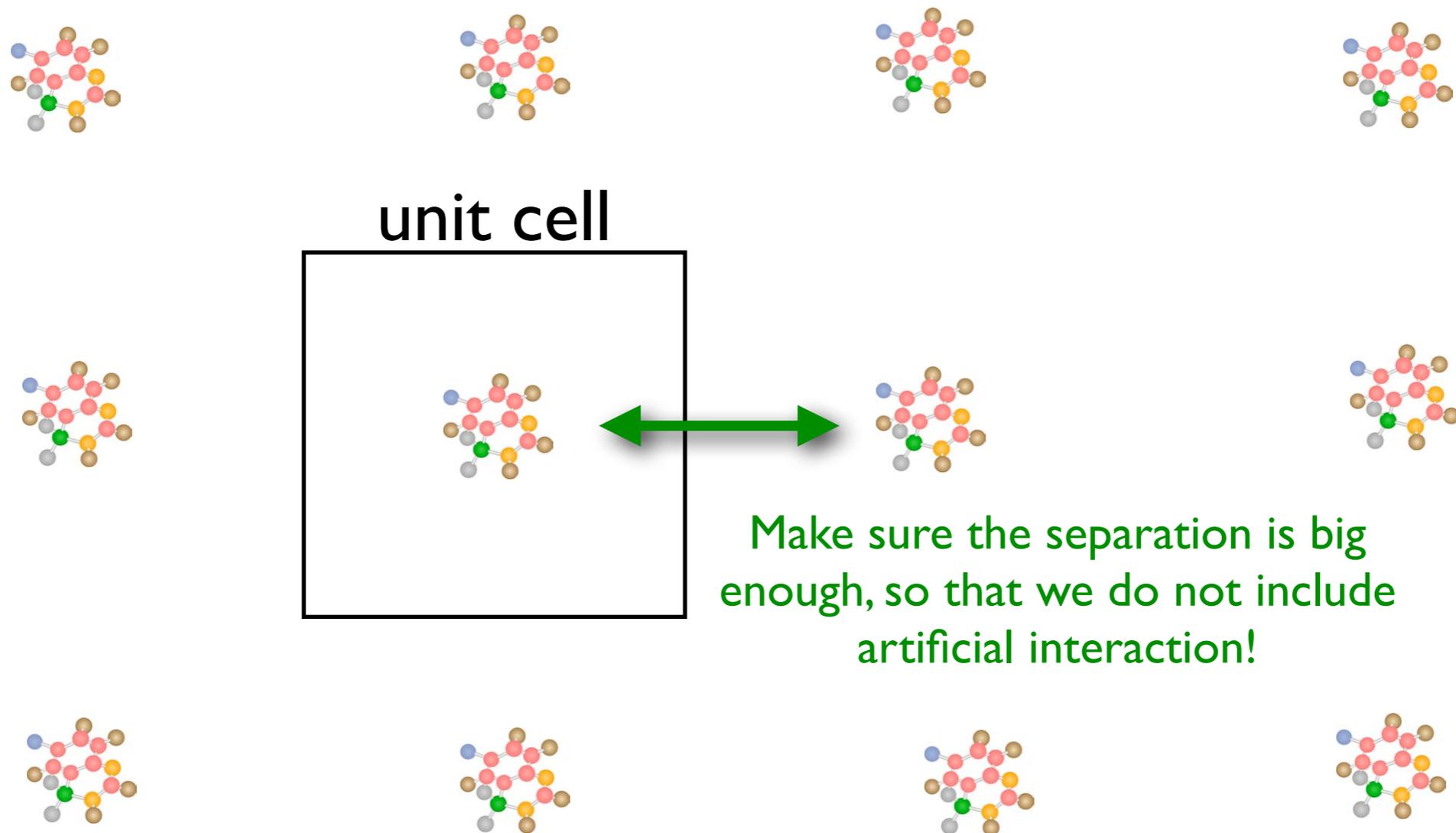thus the wave function is periodic!

periodic crystals:
Perfect!!! (next lecture)

atoms, molecules:
be careful!!!

Image by MIT OpenCourseWare.

Put molecule in a big box

unit cell

Make sure the separation is big
enough, so that we do not include
artificial interaction!

DFT calculations

scf loop

```
total energy =    -84.80957141 Ry
total energy =    -84.80938034 Ry
total energy =    -84.81157880 Ry
total energy =    -84.81278531 Ry
total energy =    -84.81312816 Ry
total energy =    -84.81322862 Ry
total energy =    -84.81323129 Ry
```

exiting loop;
result precise enough

At the end we get:

1) electronic charge density

2) total energy

- structure

- bulk modulus
                                    ❑ binding energies

- shear modulus   ❑ reaction paths

                                    ❑ forces

- elastic constants   ❑ pressure

                                    ❑ stress
- vibrational properties
                                    ❑ ...

- sound velocity

Convergence

Was my box big enough?

Was my basis big enough?

?

Did I exit the scf loop at the right point?

PWscf input

- ☐ What atoms are involved?
- ☐ Where are the atoms sitting?
- ☐ How big is the unit cell?
- ☐ At what point do we cut the basis off?
- ☐ When to exit the scf loop?

All possible parameters
are described in
INPUT_PW.

```
&control
  pseudo_dir    = ""
/

&system
  ibrav         = 1
  celldm(1)     = 15.0
  nat           = 3
  ntyp          = 2
  occupations   = 'fixed'
  ecutwfc       = 60.0
/

&electrons
  conv_thr      = 1.0d-8
/

ATOMIC_SPECIES
  H  1.00794  hydrogen.UPF
  O  15.9994  oxygen.UPF

ATOMIC_POSITIONS {bohr}
  O  0.0 0.0 0.0
  H  2.0 0.0 0.0
  H  0.0 3.0 0.0

K_POINTS {gamma}
```

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Review

- Review

- The Many-body Problem

- Hartree and Hartree-Fock

- Density Functional Theory

- Computational Approaches

- Modeling Software

- PWscf

Literature

- Richard M. Martin, Electronic Structure

- Kieron Burke, The ABC of DFT chem.ps.uci.edu/~kieron/dft/

- wikipedia, "many-body physics", "density functional theory", "pwscf", "pseudopotentials", ...

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modelling and Simulation
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